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ECBC-TR-205

HIGH ENERGY, LEAD-FREE IGNITION FORMULATION FOR THERMATE

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An efficient ignition formulation for thermate was developed during the XM89 Enhanced Incendiary Grenade program to use as an alternative to the standard lead oxide-containing formulation used in the AN-M14 thermate grenade. This lead-free formulation has provided reliable ignition of the XM89 over a temperature range of -25 °F - 120 °F when using the M201A1 fuze as the initiator. Reliable ignition of the thermate could also be achieved using 10 g of the new ignition formulation. The AN-M14 employs 30 g of ignition mix. The ignition formulation described in this report has also been successfully employed to initiate other pyrotechnic devices such as flares and smoke compositions. It may also have some application as a combination delay/output formulation in devices that do not require either a "gasless" delay or sealing of the delay tube with reaction products.

14. SUBJECT TERMS

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PREFACE

The work described in this report was authorized under Project No. 10162622A552, Smoke and Obscurants. This work was started in March 1993 and completed in September 1997.

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HIGH ENERGY, LEAD-FREE IGNITION FORMULATION FOR THERMATE

1. INTRODUCTION

The increasing awareness of toxicological problems associated with particular chemicals, in conjunction with stricter regulations governing their use, has made it desirable to replace many of the standard materials and formulations used in pyrotechnics. The standard ignition mixture (Table 1) used in the AN-M14 thermate incendiary grenade is an excellent example of a mixture that falls into this category. The drawing package for the AN-M14 specifies that 30 g of this mixture is required for each grenade. Consequently, the nominal quantity of lead oxide (Pb_3O_4) in each grenade is 7.3 g. Some of the lead produced in the reaction is vaporized when the grenade functions and the remainder solidifies in the slag and becomes a Resource Conservation Recovery Act (RCRA) hazardous solid waste.

Table 1. Standard Ignition Mixture Used in the AN-M14 Thermate Incendiary Grenade (Chemical Corps First Fire Mixture VII)

Dry Mixture

Component	Parts by Weight
Pb_3O_4	25
Fe_2O_3	25
Si	25
Ti	25

Binder

Component	Parts by Weight
Nitrocellulose	4.5 ± 0.25
Acetone	36.75 ± 1

2. DISCUSSION AND PROCEDURE

Early in the developmental phase of the XM89 Enhanced Incendiary Grenade (EIG),* the decision was made to use a lead-free ignition mixture. Table 2 lists the formulation that was initially used.

*Song, E., and Tracy, G., *Development of XM89 Enhanced Incendiary Grenade, Volume 11: Engineering Design Data/Test Report*, ECBC-TR-117, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, December 2000, UNCLASSIFIED Report.

Table 2. Initial Ignition Formulation Used in the Developmental Phase of the XM89 Enhanced Incendiary Grenade

Component	Specification	Parts by Weight
KNO_3	Mil-P-I56B Class 2, 60 mesh	66.8
Ti	Mil-T-13405 G	12.7
Al	Reynolds 40 XD Pigment Grade	8.7
Si	Amorphous	7.8
S	Jan-S-486 Grade E	2.0
Polyacrylic rubber	Zeon Chemical 4451 CG	2.0

The ignition formulation was wet mixed in a Hobart Planetary Mixer using acetone as the mixing medium. The procedure follows:

(a) The polyacrylic rubber was dissolved in a minimum quantity of acetone.

(b) The KNO_3 was passed through a #60 sieve to reduce any aggregates that might have formed.

(c) The other components of the mixture were weighed out and placed in the mixing bowl.

(d) The solution of polyacrylic rubber dissolved in acetone was added to the bowl and blended by hand until all the material was wetted.

(e) The KNO_3 was added and carefully blended by hand.

(f) Acetone was added, if necessary, to adjust the consistency of the mix to a thick slurry.

(g) After checking for proper beater clearance, the mixer was turned on.

(h) Mixing was terminated when sufficient acetone had evaporated to yield damp free, flowing powder.

(i) The powder was removed from the mixer bowl, spread on a tray, and dried in a forced air oven for a minimum of 24 hr at 140 °F.

3. RESULTS AND DISCUSSION

An extensive series of tests* using the thermate based EIG revealed a problem with low temperature (-25 °F) ignition reliability using an M201A1 fuse with a 6-s delay. This fuse had the same output as the standard M201A1 fuze, but the delay had been increased to 6 s. The ignition reliability problem at low temperature was corrected by adding a small amount of charcoal to the formulation. The resulting formulation is shown in Table 3.

Table 3. New Ignition Formulation for Thermate

Component	Specification	Parts by Weight
KNO_3	Mil-P-I56B Class 2, 60 mesh	66
Ti	Mil-T-13405 G	11
Al	Reynolds 40 XD Pigment Grade	8
Si	Amorphous	6
S	Jan-S-486 Grade E	2
Charcoal	Granulated Grade AF	5
Polyacrylic rubber	Zeon Chemical 4451 CG	2

Differential Scanning Calorimeter (DSC) analysis of this new formulation revealed that the onset of a major exotherm occurred between 420° and 462 °C, depending on the analytical parameters. Figure 1 is a sample of a DSC curve at the upper end of this range.

The thermate formulation used in this series of EIG tests was the standard formulation Chemical Corps Incendiary Mixture Thermate, TH3, Drawing B 143-13-1 with 2 parts by weight of polyacrylic rubber added. The quantity of ignition mix used in all tests of the EIG was 10 g. It was consolidated onto the end of the thermate grain with the last increment during grenade fabrication. While 10 g is one-third the quantity of the lead oxide containing First Fire VII mixture used on the AN-M14, which uses essentially the same thermate mix, the formula described in Table 3 never failed to ignite the thermate. The sensitivity to the fuze output at low temperatures was no longer a problem, and consequently, there were no failures to ignite in subsequent low temperature trials.**

Figure 2 shows the image of an EIG thermate grenade at the instant the ignition composition was initiated. This particular device used 10 g of the ignition mixture consolidated on the upper surface of a modified thermate mixture. The intense output of the ignition mixture is evident, jetting out of the vents in the top of the can.

*ECBC-TR-117, Paragraph 2.5 and Appendix C, Volume II, December 2000.
**ECBC-TR-117, Appendix D, Table D-3, Volume II, December 2000.

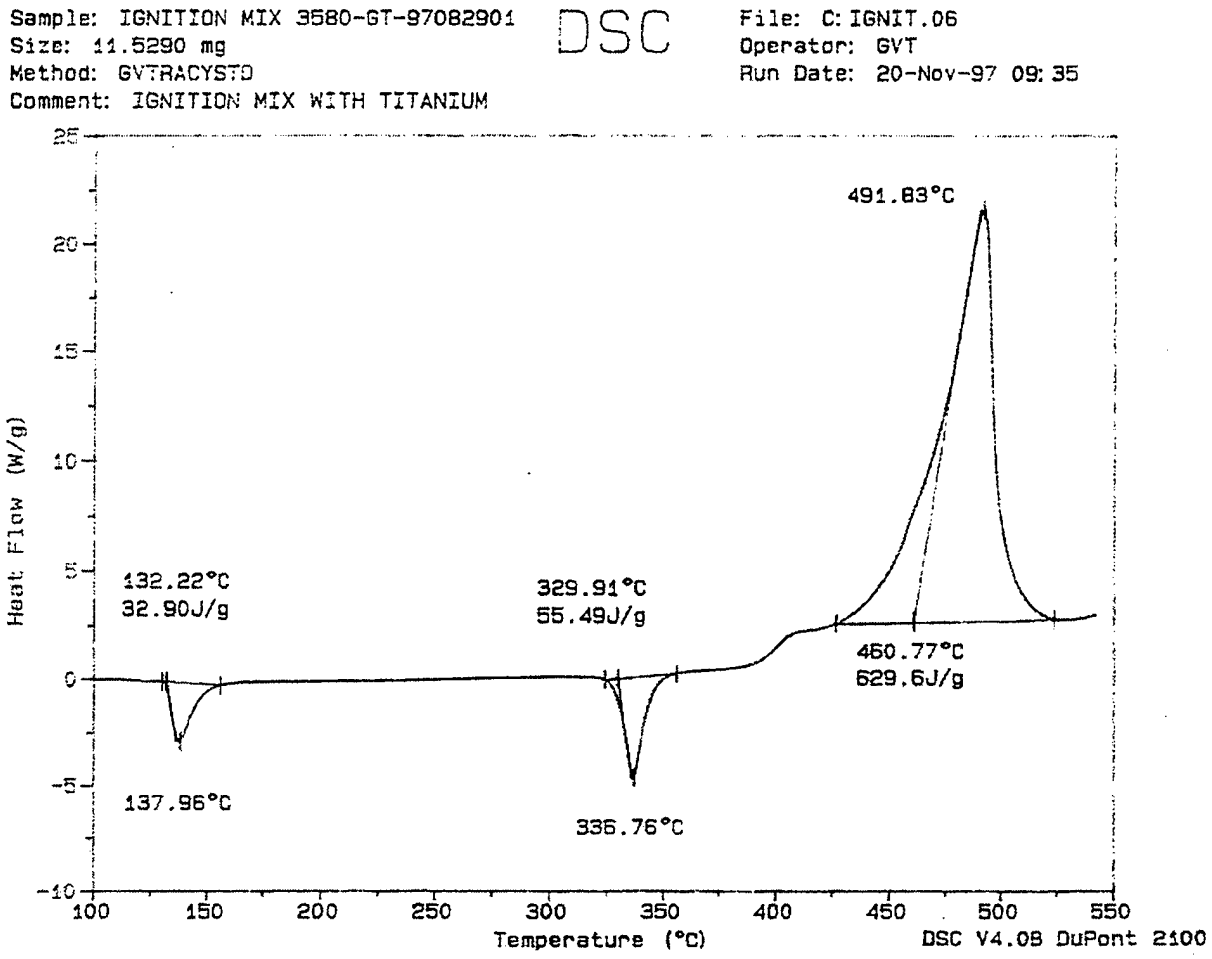

Figure 1. Differential Scanning Calorimeter Analysis of the New Ignition Formulation

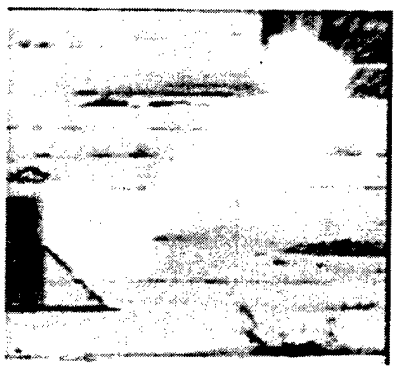

Figure 2. Enhanced Incendiary Grenade at Moment of Ignition

For comparison purposes, a theoretical analysis of the chemical reaction was carried out to calculate the heat of reaction of the new ignition formulation and the standard ignition mixture, First Fire Mixture VII based on a total mass of 100 g of initial ignition material (Appendixes A and B). The results are shown in Table 4 and Figure 3 below.

Table 4. Calculated Heat of Reaction: New Ignition Formulation Versus Standard First Fire Mixture VII

Ignition Mix	Compositions*	% by Weight	Heat of Reaction (Kcal/gm)
New Ignition Formulation	KNO_3	67.35	0.888
	Ti	11.23	
	Al	8.16	
	Si	6.12	
	S	2.04	
	C	5.10	
Standard First Fire Mixture VII	Pb_3O_4	25	0.303
	Fe_2O_3	25	
	Si	25	
	Ti	25	

*The calculation did not include the binder used in the ignition formulation.

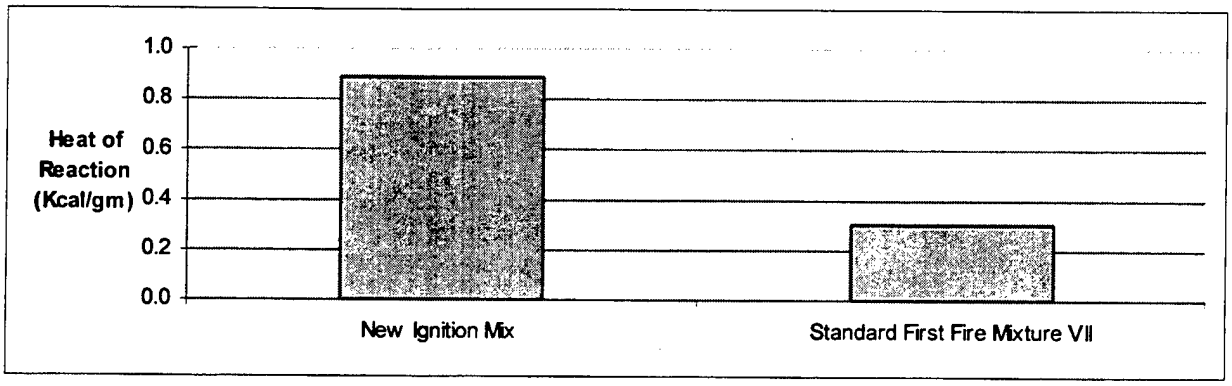

Figure 3. Calculated Heat of Reaction: New Ignition Formulation Versus Standard First Fire Mixture VII

Based on this calculation, the new ignition formulation yields almost 3 times more heat than the standard ignition mixture, or, from another perspective, the First Fire VII gives off only 34% of the heat of the new ignition formulation.

In addition to its designed function as an ignition composition for thermate, this formulation has been successfully used to initiate a wide variety of other pyrotechnics such as thermite, flare, and smoke compositions used in other projects. This formulation performed well in all of the above-mentioned applications. The formulation may be a viable alternative for other currently used ignition formulations, which contain chemicals that are no longer acceptable from a toxicity and environmental viewpoint.

This formulation has been investigated for possible use as a delay mix. A typical pyrotechnic delay assembly may contain three separate pyrotechnic materials. There is, first in the column, a "first fire" composition to receive the ignition stimulus and transfer it to the delay composition. The delay column then burns at a known rate until it contacts an output composition. The function of the output composition then is to ignite the next item in the pyrotechnic series, which is typically the material that produces the main effect. Many of the commonly encountered delay formulations contain either lead or chromate compounds that present toxicity and environmental problems. It was thought that, in some applications, the ignition mix described in this report could function in all three capacities. This would simplify design and construction of delay assemblies and, additionally, eliminate a possible source of toxic materials.

When pressed as a delay column in a brass tube with an internal diameter of 0.232 in. and a wall thickness of 0.040 in. at a pressure of 20,300 psi, the average burn rate was 8.0 s/in. The output end of the delay had a 45° conical section to enhance its performance.

Figure 4 was taken from a video recording and illustrates the output from a delay column constructed in this manner using 0.80 g of the ignition mixture. This image was taken at the end of the delay burn as the conical output portion of the delay functioned.

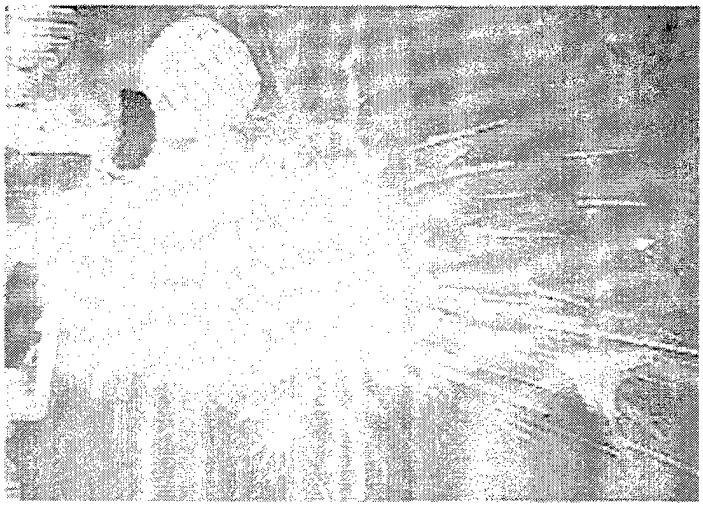

Figure 4. Output From Delay Column Pressed with Ignition Formulation

This concept was tried while developing the delay and burster assembly on an item fired from a 66 mm launcher. It was not successful in this application because the burster composition needed a high degree of confinement to function properly, and the formulation did not produce sufficient "slag" to seal the delay hole. For applications not requiring a "gasless" delay and the ability to leave a large deposit when functioning, this may still be a worthwhile concept to pursue if the burn rate of the resulting delay is suitable for the required task.

4. CONCLUSION

At the beginning of the Enhanced Incendiary Grenade (EIG) program, the decision was made not to use the lead oxide containing ignition composition that is incorporated into the AN-M14 Incendiary Grenade. The resulting formulation, described in Table 3, has proven to be an excellent composition for this task and does not contain either lead or other metallic components that are either highly toxic or detrimental to the environment. This formulation has the required sensitivity to the fuze output of an M201A1 fuze at -25 °F, the lowest temperature tested during the EIG Engineering Design Testing. The formulation has excellent thermal output and has been used in other projects to ignite various thermite compositions, as well as the more easily initiated smoke and flare compositions.

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APPENDIX A
CALCULATION OF HEAT OF REACTION
(NEW IGNITION FORMULATION)

Assumptions:

1) Compositions of Reactant Materials

	Ignition Composition						
	KNO_3	*Ti*	*Al*	*Si*	*S*	*C*	*Total*
Wt Frac	*67.35%*	*11.23%*	*8.16%*	*6.12%*	*2.04%*	*5.10%*	*100%*

2) Reactions proceeds as follows:

1 $4\ KNO_3 + 5\ Ti = 2\ K_2O + 2\ N_2 + 5\ TiO_2$

2 $6\ KNO_3 + 10\ Al = 3\ K_2O + 3\ N_2 + 5\ Al_2O_3$

3 $4\ KNO_3 + 5\ Si = 2\ K_2O + 2\ N_2 + 5\ SiO_2$

4 $4\ KNO_3 + 5\ S = 2\ K_2O + 2\ N_2 + 5\ SO_2$

5 $4\ KNO_3 + 5\ C = 2\ K_2O + 2\ N_2 + 5\ CO_2$

$\sum_{1}^{5} reaction =$

$$22\ KNO_3 + 5\ Ti + 10\ Al + 5\ Si + 5\ S + 5\ C = 11\ K_2O + 5\ TiO_2 + 5\ Al_2O_3 + 5\ SiO_2 + 5\ SO_2 + 5\ CO_2 + 11\ N_2$$

3) Composition of Reaction Products: $K_2O,\ TiO_2,\ Al_2O_3,\ SiO_2,\ SO_2,\ CO_2,\ N_2,\ C$

Material and Energy Balances:

	Basis: Reactants			100	g		
	KNO_3	Ti	Al	Si	S	C	Total
Wt Frac	67.35%	11.23%	8.16%	6.12%	2.04%	5.10%	100.00%
Mass (g)	67.35	11.23	8.16	6.12	2.04	5.10	100.00
MW	101.10	47.90	26.97	28.06	32.06	12.01	
mole, *n*	0.66617	0.23445	0.30256	0.21810	0.06363	0.42465	
St. Coeff, υ	22	5	10	5	5	5	
ΔH_f^o	-494.04	0.00	0.00	0.00	0.00	0.00	KJ/mole

	Reaction End Products				100	g			
	K_2O	TiO_2	Al_2O_3	SiO_2	SO_2	CO_2	N_2	C	Total
Wt Frac	31%	19%	15%	13%	4%	4%	9%	4%	100%
Mass (g)	31.37	18.73	15.42	13.10	4.08	3.94	9.33	4.02	100.00
MW	94.19	79.90	101.94	60.06	64.06	44.01	28.02	12.01	
mole, *n*	0.33309	0.23445	0.15128	0.21810	0.06363	0.08961	0.33309	0.33503	
St. Coeff, υ	11	5	5	5	5	5	11		
ΔH_f^o	-360.65	-895.78	-1669.76	-847.75	-296.81	-393.51	0	0	KJ/mole
Cp (460°C)	0.09291	0.06502	0.10111	0.05213	0.04498	0.04298	0.02939	0.013289	KJ/mole/°K

1 J = 0.23901 cal

Reactants

0.66617	mols	KNO3
0.23445	mols	Ti
0.30256	mols	Al
0.21810	mols	Si
0.06363	mols	S
0.42465	mols	C
	25°C	

Ignition Reaction

Products

0.33309	mols	K2O
0.23445	mols	TiO2
0.15128	mols	Al2O3
0.21810	mols	SiO2
0.06363	mols	SO2
0.08961	mols	CO2
0.33309	mols	N2
0.33503	mols	C
	460°C	

$$\Delta H = \frac{n_{AR}\,\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i H_i - \sum_{in} n_i H_i$$

$$= \frac{n_{AR}\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i Cp_i\,\Delta T - \sum_{in} n_i Cp_i\,\Delta T$$

Where

ΔH = Heat of Reaction

ΔH_r^o = Standard heat of reaction of the mix

ΔH_f^o = Standard heat of formation of species

A = Any reactant or product

n_{AR} = Moles of A either produced or consumed in the process

υ_A = Stoichiometric coefficient of A

n_i = Moles of the i^{th} component

H_i = Specific enthalpy of the i^{th} component relative to this component at 25 °C.

Cp_i = Heat capacity of the i^{th} component

Stoichiometric reaction is assumed to be

$$22\,KNO_3 + 5\,Ti + 10\,Al + 5\,Si + 5\,S + 5\,C = 11\,K_2O + 5\,TiO_2 + 5\,Al_2O_3 + 5\,SiO_2 + 5\,SO_2 + 5\,CO_2 + 11\,N_2$$

$$\Delta H_r^o = \sum_{products} \upsilon_i (\Delta H_f^o)_i - \sum_{reactants} \upsilon_i (\Delta H_f^o)_i = \quad -13{,}616.38 \quad KJ/mol$$

Basis:	100 g of pyro mix	Per g of pyro mix
$\frac{n_{AR}\,\Delta H_r^o}{\upsilon_A}$ (for 0.33309 moles of K_2O are produced) =	-412.31 KJ	-4.123 KJ/g
$\sum_{out} n_i H_i - \sum_{ii} n_i H_i = \sum_{out} n_i\,Cp_i \Delta T\,\Big\|_{25}^{460} - \sum_{in} n_i Cp_i \Delta T\,\Big\|_{25}^{25} =$	40.81 KJ	0.408 KJ/g
$\Delta H = \frac{n_{AR}\,\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i H_i - \sum_{in} n_i H_i =$	-371.50 KJ	-3.715 KJ/g
	-88.79 Kcal	-0.888 Kcal/g

APPENDIX B
CALCULATION OF HEAT OF REACTION
(STANDARD IGNITION MIXTURE, FIRST FIRE MIXTURE VII)

Assumptions:

1) Compositions of Reactant Materials

	Ignition Composition				
	Pb_3O_4	Fe_2O_3	*Si*	*Ti*	*Total*
Wt Frac	*25%*	*25%*	*25%*	*25%*	*100%*

2) Reactions proceeds as follows:

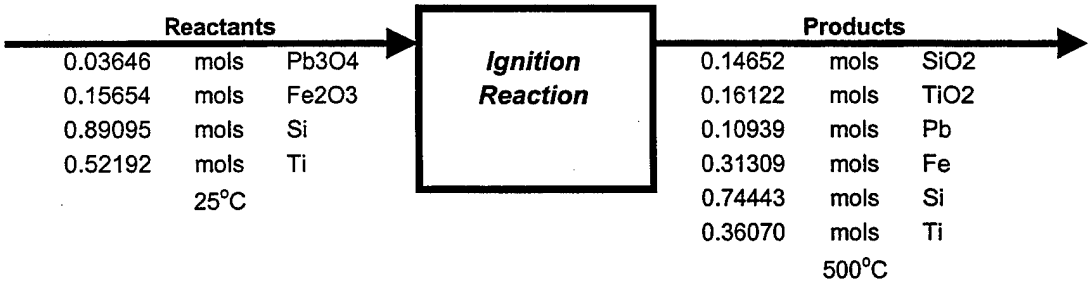
1	$Pb_3O_4 + 2\,Ti = 2\,TiO_2 + 3\,Pb$
2	$2\,Fe_2O_3 + 3\,Si = 3\,SiO_2 + 4\,Fe$
3	$Pb_3O_4 + 2\,Si = 2\,SiO_2 + 3\,Pb$
4	$2\,Fe_2O_3 + 3\,Ti = 3\,TiO_2 + 4\,Fe$
Total	$2\,Pb_3O_4 + 4\,Fe_2O_3 + 5\,Si + 5\,Ti = 5\,SiO_2 + 5\,TiO_2 + 6\,Pb + 8\,Fe$

3) Composition of Reaction Products: SiO_2, TiO_2, *Pb, Fe, Si, Ti*

Material and Energy Balances:

	Basis: Reactants			100	g
	Pb_3O_4	Fe_2O_3	*Si*	*Ti*	Total
Wt Frac	25%	25%	25%	25%	100%
Mass (g)	25.00	25.00	25.00	25.00	100.00
MW	685.63	159.70	28.06	47.90	
mole, *n*	0.03646	0.15654	0.89095	0.52192	
St. Coeff, υ	2	4	5	5	
ΔH_f°	-721.31	-830.51	0.00	0.00	KJ/mole

	Reaction End Products				100	g	
	SiO_2	TiO_2	Pb	Fe	Si	Ti	Total
Wt Frac	9%	13%	23%	17%	21%	17%	100%
Mass (g)	8.80	12.88	22.67	17.49	20.89	17.28	100.00
MW	60.06	79.90	207.21	55.85	28.06	47.90	
mole, *n*	**0.146520**	**0.161220**	0.109388	0.313087	**0.744430**	**0.360700**	
	a	**b**			**c**	**d**	
St. Coeff, υ	5	5	6	8			
ΔH_f°	-847.75	-895.78	0.00	0.00	0.00	0.00	KJ/mole
Cp (500°C)	0.05213	0.06502	0.03063	0.02970	0.02415	0.02860	KJ/mole/°K
					1 J =	0.23901	cal



Atomic Balance

Si	0.89095	= a + c							
Ti	0.52192	= b + d							
O	0.6154818	= 2a + 2b	⟶	0.30774	= a + b				
Total Mass	100.00	= 60.06a + 79.90 b +		207.21 x	0.10939	+ 55.85 x	0.31309	+ 28.06 c	+ 47.90 d

Solving for Constant a, b, c using Matrix Determinant Method

a	b	c	d			
1		1		0.89	with	
	1		1	0.52	Formula	
1	1			0.31		
2.14	2.85	1.00	1.71	2.13		

MDETERM (Matrix Determinant)

a	b	c	d		with	|A|
1	0	1	0	0.89	Constant	1.00E-01
0	1	0	1	0.52		
1	1	0	0	0.31		
2.1	2.90	1	1.7	2.13		

a	b	c	d	MDETERM |a|	Value $a = \frac{\lvert a \rvert}{\lvert A \rvert}$
0.89	0	1	0	0.014652	**0.14652**
0.52	1	0	1		
0.31	1	0	0		
2.13	2.90	1	1.7		

a	b	c	d	|b|	$b = \frac{\lvert b \rvert}{\lvert A \rvert}$
1	0.89	1	0	0.016122	**0.16122**
0	0.52	0	1		
1	0.31	0	0		
2.1	2.13	1	1.7		

a	b	c	d	|c|	$c = \frac{\lvert c \rvert}{\lvert A \rvert}$
1	0	0.89	0	0.074443	**0.74443**
0	1	0.52	1		
1	1	0.31	0		
2.1	2.90	2.13	1.7		

a	b	c	d	|d|	$d = \frac{\lvert d \rvert}{\lvert A \rvert}$
1	0	1	0.89	0.03607	**0.3607**
0	1	0	0.52		
1	1	0	0.31		
2.1	2.90	1	2.13		

$$\Delta H = \frac{n_{AR}\,\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i H_i - \sum_{in} n_i H_i$$

$$= \frac{n_{AR}\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i Cp_i\,\Delta T - \sum_{in} n_i Cp_i\,\Delta T$$

Where

ΔH = Heat of Reaction

ΔH_r^o = Standard heat of reaction of the mix

ΔH_f^o = Standard heat of formation of species

A = Any reactant or product

n_{AR} = Moles of A either produced or consumed in the process

υ_A = Stoichiometric coefficient of A

n_i = Moles of the i^{th} component

H_i = Specific enthalpy of the i^{th} component relative to this component at 25 °C.

Cp_i = Heat capacity of the i^{th} component

Stoichiometric reaction is assumed to be

$$2\,Pb_3O_4 + 4\,Fe_2O_3 + 5\,Si + 5\,Ti = 5\,SiO_2 + 5\,TiO_2 + 6\,Pb + 8\,Fe$$

$$\Delta H_r^o = \sum_{products} \upsilon_i (\Delta H_f^o)_i - \sum_{reactants} \upsilon_i (\Delta H_f^o)_i = \quad -3{,}952.97 \quad KJ/mol$$

Basis:	100 g of pyro mix	Per g of pyro mix
$\frac{n_{AR}\,\Delta H_r^o}{\upsilon_A}$ (for 0.31309 moles of Fe are produced) =	-154.70 KJ	-1.547 KJ/g
$\sum_{out} n_i H_i - \sum_{il} n_i H_i = \sum_{out} n_i\,Cp_i \Delta T\,\Big|_{25}^{500} - \sum_{in} n_i Cp_i \Delta T\,\Big|_{25}^{25} =$	28.06 KJ	0.281 KJ/g
$\Delta H = \frac{n_{AR}\,\Delta H_r^o}{\upsilon_A} + \sum_{out} n_i H_i - \sum_{in} n_i H_i =$	-126.65 KJ	-1.266 KJ/g
	-30.27 Kcal	-0.303 Kcal/g